

DECLARATION

I, Masaya YOSHIDA, of S SOGA & CO, 8th Floor Kokusai Building, 1-1, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, declare that I am conversant with the English and Japanese languages, and that, to the best of my knowledge and belief, the attached document is a faithful translation of the document filed in connection with Japanese Patent Application No 2002-359525 filed on December 11, 2002

Place Tokyo, Japan

Dated this 14 th day of October, 2005.

Masava YOSHIDA



[NAME OF DOCUMENT]

Patent Application

[REFERENCE NUMBER]

542036JP01

[FILING DATE]

December 11, 2002

[ADDRESSEE]

The Commissioner of the Patent Office

[INTERNATIONAL CLASSIFICATION] HOLL 21/00

[INVENTOR]

[DOMICILE OR RESIDENCE] c/o Mitsubishi Denki Kabushiki Kaisha,

2-3, Marunouchi 2-chome, Chiyoda-ku, Tokyo

Noboru MIKAMI

[INVENTOR]

[NAME]

[DOMICILE OR RESIDENCE] c/o Tri Chemical Laboratories Inc.

8154-217, Uenohara, Uenohara-machi,

Kitatsuru-gun, Yamanasni 409-0112 Japan

[NAME] Hideaki MACHIDA

[PATENT APPLICANT]

[IDENTIFICATION NUMBER] 000006013

[NAME OR TITLE] Mitsubishi Denki Kabushiki Kaisha

[PATENT APPLICANT]

[IDENTIFICATION NUMBER] 591006003

[NAME OR TITLE] Tri Chemical Laboratories Inc.

[AGENT]

[IDENTIFICATION NUMBER] 100057874

[PATENT ATTORNEY]

[NAME OR TITLE] Michiteru SOGA

[APPOINTED AGENT]

[IDENTIFICATION NUMBER] 100110423

[PATENT ATTORNEY]

[NAME OR TITLE] Michiharu SOGA

[APPOINTED AGENT]

[IDENTIFICATION NUMBER] 100084010

[PATENT ATTORNEY]

[NAME OR TITLE] Hidetoshi FURUKAWA

[APPOINTED AGENT]

[IDENTIFICATION NUMBER] 100094695

[PATENT ATTORNEY]

[NAME OR TITLE] Norikazu SUZUKI

[APPOINTED AGENT] [IDENTIFICATION NUMBER] 100111648 [PATENT ATTORNEY] Jun KAJINAMI [NAME OR TITLE] (FEES) [PREPAYMENT REGISTRATION NUMBER] 000181 21,000 Yen [AMOUNT OF PAYMENT] [CATALOGUE OF ARTICLE FILED] Specification [NAME OF ARTICLE] Drawings [NAME OF ARTICLE] Abstract [NAME OF ARTICLE] [PROOF REQUIRED OR NOT] Required



[TITLE OF DOCUMENT] SPECIFICATION

[TITLE OF INVENTION] AN UNDERLAYER FILM-FORMING MATERIAL FOR COPPER, METHOD FOR A FORMING UNDERLAYER FILM FOR COPPER, AN UNDERLAYER FILM FOR COPPER, AND A SEMICONDUCTOR DEVICE

[SCOPE OF CLAIMS]

[CLAIM 1] An underlayer film-forming material for copper, characterized by comprising a compound represented by the following general formula [I].

General formula [I]

 $(R_1R_2)P-(R)_n-Si(X_1X_2X_3)$

[wherein at least one of X_1 , X_2 , and X_3 represents a hydrolysable group; R_1 and R_2 each represent an alkyl group; R represents a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.]

[CLAIM 2] An underlayer film-forming material for copper according to claim 1, wherein in the general formula [I], at least one of X_1 , X_2 , and X_3 is selected from a group consisting of a halogen, an alkowide group, an amino group and an isocyanate group; R_1 and R_2 represent an alkyl group having 1 to 21 carbon atoms; R is a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring, each of which has 1 to 50 carbon atoms; and n represents an integer of 1 to 6.

[CLAIM 3] An underlayer film-forming material for copper according to claim 1, characterized by comprising a compound and a solvent.

[CLAIM 4] An underlayer film-forming material for copper according to claim 1, characterized in that the compound represented by the general formula [I] is at least one compound selected from the group consisting of 1-dimethylphosphino-2-triethoxysilylethane,

- l-diethylphosphino-2-triethoxysilylethane,
- 1-diphenylphosphino-2-triethoxysilylethane,
- 1-dimethylphosphino-2-trimethoxysilylethane,
- 1-diethylphosphino-2-trimethoxysilylethane,
- 1-diphenylphosphino-2-trimethoxysilylethane,
- 1-dimethylphosphino-3-triethoxysilylpropane,
- 1-diethylphosphino-3-triethoxysilylpropane.
- 1-diphenylphosphino-3-triethoxysilylpropane,
- 1-diphenylphosphino-2-trichlorosilylethane,
- 1-diphenylphosphino-2-trisdimethylaminosilylethane.
- 1-diphenylphosphino-2-triisocyanatesilylethane, and
- 1-diphenylphosphino-4-triethoxysilylethylbenzene.
- [CLAIM 5] A method for forming an underlayer film for copper, characterized by comprising a process of bringing an underlayer film-forming material for copper including a compound represented by the following general formula [I] into contact with a surface of a substrate.

General formula [I]

 $(R_1R_2)P-(R)_n-S1(X_1X_2X_3)$

[wherein at least one of X_1 , X_2 , and X_3 represents a hydrolysable group; R_1 and R_2 each represent an alkyl group; R represents a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.]

[CLAIM6] Amethodfor forming a underlayer film for copper according to claim 5, characterized in that the underlayer film for copper is formed such that the $(R_1R_2)P-(R)_n$ -Si group thereof bonds to the substrate via a Si-O bond, and the underlayer film for copper is formed by a reaction between -OH on the surface of the substrate and -Si($X_1X_2X_3$) in a liquid phase.

[CLAIM 7] A method for forming an underlayer film for copper according to claim 5, characterized in that the underlayer film for copper is formed such that the $(R_1R_2)P-(R)_n$ -Si group thereof bonds to the substrate via a Si-O bond, and the underlayer film for copper is formed by a reaction in a gas phase between -OH on the surface of the substrate and $-Si(X_1X_2X_3)$.

[CLAIM 8] A method for forming an underlayer film for copper according to claim 5, characterized in that the underlayer film for copper is formed such that the $(R_1R_2)P-(R)_n$ -Si group thereof bonds to the substrate via a Si-O bond, and the underlayer film for copper is formed by a reaction in a supercritical fluid between -OH on the surface of the substrate and $-Si(X_1X_2X_3)$.

[CLAIM 9] A method for forming an underlayer film for copper according to claim 5. characterized in that the reaction between -OH on the surface of the substrate and $-S1(X_1X_2X_3)$ is carried out at a temperature of room temperature to 450° C.

[CLAIM 10] A method for forming an underlayer film for copper according to any of claims 5 to 9, characterized by further comprising a process of removing by-product(s) produced in the reaction between -OH on the surface of the substrate and $-Si(X_1X_2X_3)$.

[CLAIM 11] An underlayer film for copper arranged on a substrate, characterized in that the film is formed such that a $(R_1R_2)P$ - $(R)_n$ -Si group bonds to a substrate via a Si-O bond, wherein R_1 and R_2 each represent an alkyl group; R represents a divalent linear organic group formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.

[CLAIM 12] An underlayer film for copper according to claim 11, characterized in that the film is formed by a method for forming an underlayer film for copper including a process of bringing an underlayer film-forming material for copper including a compound represented by the following general formula [I] into contact with a surface of a substrate.

General formula [I]

 $(R_1R_2)P-(R)_n-Si(X_1X_2X_3)$

[wherein at least one of X_1 , X_2 , and X_3 represents a hydrolysable

group; R_1 and R_2 each represent an alkyl group; R represents a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.]

[CLAIM 13] A semiconductor device comprising: a substrate; an underlayer film for copper arranged on the substrate; and a wiring film made up mainly of copper and arranged on the underlayer film for copper, wherein the underlayer film for copper is formed such that a $(R_1R_2)P-(R)_n-Si$ group bonds to a substrate via a Si-O bond. [wherein R_1 and R_2 each represent an alkyl group; R represents a divalent linear organic group formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.]

[DETAIL DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF THE INVENTION]

The present invention relates to an underlayer film-forming material for copper, a method for forming a copper underlayer film, an underlayer film for copper, and a semiconductor device, and more specifically to an underlayer film-forming material for copper, a method for forming an underlayer film for copper, an underlayer film for copper, and a semiconductor device, which can prevent copper diffusion even when the thickness of the underlayer film is thinner than that of conventional barrier metals, and which enable superior

adhesion to copper wiring film.

[0002]

[PRIOR ART]

In recent years, the development of LSI technology has been significant, and the size of LSIs is becoming even-smaller. Thus, the width of wiring through which signals are transmitted is also getting smaller, i.e., wirings are becoming ultrathin. As the resistance values of conventional Tungsten (W) film and Aluminium (Al) film are said to be unable to withstand this thinning of the wire, the adoption of copper (Cu), which has a low resistance value, has been suggested.

However, the adoption of copper film, with its lower resistivity causes several problems that do not occur in the case of adopting WorAlfilm. One problem is that copper diffuses to the circumference of the LSI, and when this happens the function of the LSI is largely lost.

Therefore, a method was proposed for forming an alloy film for preventing copper diffusion (a barrier metal: TiN, TaW, ZrN, VN, TiSiN, etc.) as an underlayer film on a substrate (for example, see nonpatent document 1).

There is, however, a lower limit on the thickness of such alloy film that allows the alloy film to efficiently function as a barrier metal. If the thickness is below the lower limit, the alloy film does not function as a barrier metal. On the other hand, the width

of copper wiring film is predicted to fall below 0.1 µm in the future. Therefore, if the thickness of the barrier metal cannot be further reduced, the thickness of the copper wiring film alone will have to be reduced, and when this is coupled with the prediction that the width of the copper wiring film will be under 0.1 µm in the future, the cross-sectional area of the copper wiring film will become too small, which makes the adoption of copper with low resistivity meaningless. In other words, the limitations of alloy films such as mentioned above are becoming apparent.

Another problem is that the adhesion of conventional barrier metals to copper is inferior. For example, a copper film (a plated copper film or a CVD copper film) readily peels off from either a Si or SiO₂ underlayer film. In particular, the adhesion characteristics between a copper film and an underlayer film are reported to be worst in the case where a Tantalum(Ta)-based film, which is considered to be the most efficient of the above-mentioned barrier metals is arranged as the underlayer film. In this case, the copper film may even peel off as it forms on the Ta-based film.

[NONPATENT DOCUMENT 1] "The latest developments in copper wiring technology". Realize Corporation, May 30th, 1998, pp. 3-171

[0003]

[PROBLEMS IN WHICH THE INVENTION INTENDS TO SOLVE]

Therefore, it is an object of the present invention to solve

the problems such as those mentioned above which exist in conventional barrier metals, and to provide an underlayer film-forming material for copper, a method for forming an underlayer film for copper, an underlayer film for copper, and a semiconductor device, which enable the prevention of copper diffusion even if the thickness of underlayer film is thinner than that of conventional barrier metals, and which enable superior adhesion to copper wiring film.

[0005]

[MEAN TO SOLVE THE PROBLEMS]

The inventor of the present invention has carried out extensive research and development to solve the above problems, and has discovered that a molecular film made of organophosphorus-silicon based $[(R_1R_2)P-(R)_n-Si-O-]$, which will be explained hereinafter, prevents copper diffusion even with a thickness of several tens of Å and has superior adhesion to copper film.

[0006]

Therefore, according to the present invention, there is provided an underlayer film-forming material for copper, characterized by containing a compound represented by the following general formula [1].

General formula [I]

 $(R_1R_2)P-(R)_n-Si(X_1X_2X_3)$

[In the general formula [I], at least one of X_1 , X_2 , and X_3 represents a hydrolysable group; each of R_1 and R_2 represents an alkyl group;

R represents a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.]

[0007]

Further, according to the present invention, there is provided a method for forming an underlayer film for copper, characterized by including a process of bringing an underlayer film-forming material for copper containing the compound represented by the above general formula [I] into contact with a surface of a substrate.

[8000]

Further, according to the present invention, there is provided an underlayer film for copper, arranged on a substrate, characterized in that the underlayer film for copper is formed such that a $(R_1R_2)P-(R)n-Si$ group bonds to a substrate via a Si-O bond. [Note that in the above formula, R_1 , R_2 , R, and n are defined in the same manner as described above.]

[0009]

Further, according to the present invention, there is provided a semiconductor device equipped with: a substrate; an underlayer film for copper arranged on the substrate; and a wiring film made up mainly of copper arranged on said underlayer film for copper, with said semiconductor device characterized in that the underlayer film for copper is formed such that a $(R_1R_2)P-(R)_n-Si$ group bonds to the substrate via a Si-O bond.

[Note that in the above formula, R_1 , R_2 , R, and n are defined in the same manner as described above.]

[0010]

[DESCRIPTION OF THE PREFERRED EMBODIMENT]

An underlayer film-forming material for copper wiring film according to the present invention contains a compound represented by the following general formula [I].

General formula [I]

 $(R_1R_2)P-(R)_n-Si(X_1X_2X_3)$

In the above general formula [I], at least one of X_1 , X_2 , and X_3 represents a hydrolysable group; each of R_1 and R_2 represents an alkyl group; R represents a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.

The compound represented by the above general formula [I] is a hydrolysable compound which reacts with -OH on the surface of a substrate to generate a free HX and a $[(R_1R_2)P-(R)_n-Si-O-substrate)].$

In the above general formula [I], X_1 , X_2 , and X_3 are preferably selected from the group consisting of a halogen, an alkoxide group, an amino group and an isocyanate group respectively.

Further, for each of R_1 and R_2 it is particularly preferably for their alkyl groups to have 1 to 21 carbon atoms. Of these, alkyl

groups each having 1 to 14 carbon atoms are more preferable.

Further, for R it is particularly preferable for the group to have 1 to 50 carbon atoms. Of these, a group having 1 to 5 carbon atoms is more preferable.

[0011]

Among the compounds represented by the general formula [I], 1-dimethylphosphino-2-triethoxysilylethane,

- 1-diethylphosphino-2-triethoxysilylethane,
- 1-diphenylphosphino-2-triethoxysilylethane,
- 1-dimethylphosphino-2-trimethoxysilylethane,
- 1-diethylphosphino-2-trimethoxysilylethane,
- 1-diphenylphosphino-2-trimethoxysilylethane,
- 1-dimethylphosphino-3-triethoxysilylpropane,
- l-diethylphosphino-3-triethoxysilylpropane,
- 1-diphenylphosphino-3-triethoxysilylpropane,
- l-diphenylphosphino-2-trichlorosilylethane,
- 1-diphenylphosphino-2-trisdimethylaminosilylethane,
- 1-diphenylphosphino-2-triisocyanatesilylethane, and
- 1-diphenylphosphino-4-triethoxysilylethylbenzene are preferable.

[0012]

A method for forming an underlayer film for copper according to the present invention is a method for forming an underlayer film for copper on a substrate to be provided with a copper film, in which the above underlayer film-forming material for copper comes in contact with a surface of the substrate. In particular, the method according to the present invention is a method for forming an underlayer film for copper wiring film on a substrate to be provided with copper wiring film, the method including a process of bringing the above underlayer film-forming material for copper into contact with a surface of the substrate, preferably further including a process of removing reaction by-product(s) generated during the preceding process from the surface of the substrate.

The underlayer film for copper according to the present invention, for example, is formed such that the $(R_1R_2)P$ - $(R)_n$ -Si group thereof bonds to the substrate via a Si-O bond. Such a structure may be obtained by immersing the substrate into a solution containing a compound represented by the general formula [I] and a solvent. The compound is preferably incorporated into the solution at a concentration of about 1% by volume.

Immersing the substrate into the solution containing the compound represented by the general formula [I] leads to a reaction in a liquid phase between -OH on the surface of the substrate and $-\text{Si}(X_1X_2X_3)$ of the above compound, to readily yield a substrate to which a $(R_1R_2)P-(R)_n-\text{Si}$ group bonds via a Si-O bond.

Alternatively, a gas phase method may be used instead of the liquid phase method. For example, transporting the above compounds to the surface of the substrate by CVD also leads to the reaction in a gas phase between -OH on the surface of the substrate and

 $-Si(X_1X_2X_3)$ of the above compound, to readily yield a substrate to which a $(R_1R_2)P-(R)_n-Si$ group bonds via a Si-O bond.

Furthermore, a method other than the above is as follows. Adding the above compound into a supercritical fluid and then introducing a substrate into said fluid also readily yields a substrate to which a $(R_1R_2)P-(R)_n-Si$ group bonds via a Si-O bond.

Note that the reaction between -OH on the surface of the substrate and -S1($X_1X_2X_3$) is, for reaction efficiency, preferably carried out at conditions from room temperature (e.g., 25°C) to 450°C.

[0013]

Note that the process of removing reaction by-products from the surface of the substrate may be performed by, for example, washing the substrate using the same solvent as the reaction solvent to remove the by-product(s) produced in the reaction between -OH on the surface of the substrate and $-S1(X_1X_2X_3)$, and further baking the substrate to remove the residual solvent.

[0014]

Further, the underlayer film for copper according to the present invention is formed such that a $(R_1R_2)P-(R)_n$ -Si group bonds to the substrate via a Si-O bond. The underlayer film for copper may be obtained easily in accordance with the above-described method for forming underlayer film for copper of the present invention.

The thickness of the underlayer film for copper is, for example, 1 to 3 nm.

[0015]

A semiconductor device according to the present invention is equipped with: a substrate; an underlayer film for copper arranged on the substrate; and a wiring film made up mainly of copper and provided on the underlayer film for copper, and in the semiconductor device, the underlayer film for copper is formed such that a $(R_1R_2)P-(R)_0$ -Si group bonds to the substrate via a Si-O bond.

[0016]

[EXAMPLES]

Hereinafter the present invention will be explained in more detail with reference to the examples.

EXAMPLE 1

A silicon substrate with a SiO_2 thermal oxide film formed on its surface was used as a substrate. The substrate, having its surface subjected to a Si-OH termination treatment, was immersed into a 1% by volume toluene solution of

1-diphenylphosphino-2-triethoxysilylethane heated to 60°C for 1 hour. After 1 hour, the substrate was taken out of the solution, washed with toluene, and dried. Subsequently, the substrate was heated at 120°C for 4 minutes to remove the residual solvent and byproduct.

The surface of the substrate obtained as above was measured using a reflectometer. The measurement showed that a nearly uniform thin film having a thickness of 1.2 nm was formed.

While measuring the thin film using FT-IR, peaks corresponding to Ph₂PCH₂CH₂SiO- (where Ph represents a phenyl group) were observed.

After the formation of the thin film, a copper thin film having a thickness of 100 nm was formed by the CVD method using a hexafluoracetylacetonate copper trimethylvinylsilane adduct as a source material.

The copper thin film was subjected to a tape peeling test to determine adhesion to the underlayer film. In contrast to the copper thin film peeling off in the case of conventional barrier metals. in this example no peeling was observed.

The substrate was also subjected to the Back side SIMS to determine the copper diffusion to the underlayer film although no copper diffusion was observed.

[0017]

EXAMPLES 2-13

The procedure of Example 1 was repeated except that, instead of 1-dimethylphosphino-2-triethoxysilylethane used in Example 1, 1-dimethylphosphino-2-triethoxysilylethane (Example 2), 1-diethylphosphino-2-triethoxysilylethane (Example 3), 1-dimethylphosphino-2-trimethoxysilylethane (Example 4). 1-diethylphosphino-2-trimethoxysilylethane (Example 5), 1-diphenylphosphino-2-trimethoxysilylethane (Example 6), 1-dimethylphosphino-3-triethoxysilylpropane (Example 7), 1-diethylphosphino-3-triethoxysilylpropane (Example 8).

l-diphenylphosphino-3-triethoxysilylpropane (Example 9),
l-diphenylphosphino-2-trichlorosilylethane (Example 10),
l-diphenylphosphino-2-trisdimethylaminosilylethane (Example 11),
l-diphenylphosphino-2-triisocyanatesilylethane (Example 12), and
l-diphenylphosphino-4-triethoxysilylethylbenzene (Example 13)

As a result, a thin film having a thickness of 1.2 to 2.2 nm in which a $(R_1R_2)P^-(R)_n$ -Si group bonds to the substrate via a Si-O bond was formed in each of the examples. The adhesion of the copper thin film was examined for each example using the tape peeling test. In the test, peeling of the copper thin film was not observed in any of the examples. The copper diffusion to the underlayer film was also examined using the Back side SIMS for each example, but no copper diffusion was observed in any of the examples.

[0018]

were used.

EXAMPLES 14-26

Instead of the silicon substrate a S1O₂ thermal oxidation film formed on its surface, a silicon substrate having an alkylsilicon-based film with a low dielectric constant was used in each of Examples 1 to 13, and was subjected to a similar process as above.

As a result, a thin film having a thickness of 1.2 to 2.2 nm in which a $(R_1R_2)P-(R)_n$ -Si group bonds to the substrate via a Si-O bond was formed in each of the examples. The adhesion of the copper

thin film was examined for each example using the tape peeling test. In the test, peeling of the copper thin film was not observed in any of the examples. The copper diffusion to the underlayer film was also examined using the Back side SIMS for each example, but no copper diffusion was observed in any of the examples.

[0019]

EXAMPLE 27

Fig. 1 is a schematic view for illustrating a film-forming apparatus (MOCVD). In Fig. 1, the film-forming apparatus includes source material containers la and 1b, a heater 3, a decomposition reactor 4, a substrate 5, gas flow controllers 7, and a gas blowout shower head 9.

The source material container la contains

1-dimethylphosphino-2-trimethoxysilylethane kept at 90°C. The sourcematerial container lb contains water kept at room temperature. Argon serving as a carrier gas was introduced into the source material containers la and lb at a rate of 1 to 10 ml/min respectively. The pressure in the decomposition reactor 4 was kept at 1 to 100 Pa, and the temperature of the substrate 5 was kept at 40 to 200°C. The film formation was carried out by introducing water vapor to the decomposition reactor 4 to hydroxylate the surface of the substrate, followed by introducing vapor of

1-dimethylphosphino-2-trimethoxysilylethane to the reactor.

The surface of the substrate 5 obtained as above was measured

using a reflectometer. The measurement showed that a nearly uniform thin film having a thickness of 1.2 nm was formed.

In examining the thin film using FT-IR, peaks corresponding to (Me)2PCH2CH2SiO- (where Me represents a methyl group) were observed.

After the formation of the thin film, a copper thin film having a thickness of 140 nm was formed by the CVD method using a hexafluoracetylacetonate copper trimethylvinylsilane adduct as a source material.

The copper thin film was subjected to a tape peeling test to determine adhesion to the underlayer film. In contrast to the copper thin film peeling off in the case of conventional barrier metals. in this example no peeling was observed.

The substrate was also subjected to the Back side SIMS to determine the copper diffusion to the underlayer film although no copper diffusion was observed.

Alternatively, a silicon substrate including an alkylsilicon-based film with a low dielectric constant was subjected to a similar process and similar tests, instead of the above silicon substrate. The silicon substrate showed similar results as above.

[0020]

EXAMPLES 28-39

The procedure of Example 27 was repeated in each of Examples 28 to 39 except that, instead of

```
1-diphenylphosphino-2-triethoxysilylethane used in example 27,
1-dimethylphosphino-2-triethoxysilylethane (Example 28),
1-diethylphosphino-2-triethoxysilylethane (Example 29),
1-dimethylphosphino-2-trimethoxysilylethane (Example 30),
1-diethylphosphino-2-trimethoxysilylethane (Example 31),
1-diphenylphosphino-2-trimethoxysilylethane (Example 32),
1-dimethylphosphino-3-triethoxysilylpropane (Example 33),
1-diethylphosphino-3-triethoxysilylpropane (Example 34),
1-diphenylphosphino-3-triethoxysilylpropane (Example 35),
1-diphenylphosphino-2-trichlorosilylethane (Example 36),
1-diphenylphosphino-2-trisdimethylaminosilylethane (Example 37),
1-diphenylphosphino-2-triisocyanatesilylethane (Example 38), and
1-diphenylphosphino-4-triethoxysilylethylbenzene (Example 39)
were used.
```

As a result, a thin film having a thickness of 1.2 to 2.2 nm in which a $(R_1R_2)P^-(R)_n$ -Si group bonds to the substrate via a Si-O bond was formed in each of the examples. The adhesion of the copper thin film was examined for each example using the tape peeling test. In the test, peeling of the copper thin film was not observed in any of the examples. The copper diffusion to the underlayer film was also examined using the Back side SIMS for each example, but no copper diffusion was observed in any of the examples.

[0021]

EXAMPLE 40

A silicon substrate with a Sio₂ thermal oxidation film formed on its surface was used as a substrate. The substrate having the surface subjected to a Si-OH termination treatment was placed in the reactor, and was reacted in contact with a 1% by volume of CO₂ supercritical fluid of 1-diphenylphosphino-2-triethoxysililethane heated to 60°C. After 1 hour, the substrate was washed with a CO₂ supercritical fluid still in the reactor, and was further heated in the CO₂ supercritical fluid at 120°C for 4 minutes.

The surface of the substrate obtained as above was measured using a reflectometer. The measurement showed that a nearly uniform thin film having a thickness of 1.2 nm was formed.

In examining the thin film using FT-IR, peaks corresponding to $Ph_2PCH_2CH_2SiO$ - were observed.

After the formation of the thin film, a copper thin film having a thickness of 100 nm was formed by the CVD method using a hexafluoracetylacetonate copper trimethylvinylsilane adduct as a source material.

The copper thin film was subjected to a tape peeling test to determine adhesion to the underlayer film. In contrast to the copper thin film peeling off in the case of conventional barrier metals, in this example no peeling was observed.

The substrate was also subjected to the Back side SIMS to determine the copper diffusion to the underlayer film although no copper diffusion was observed.

[0022]

[ADVANTAGEOUS EFFECT OF THE INVENTION]

According to the present invention, there is provided an underlayer film-forming material for copper, a method for forming an underlayer film for copper, an underlayer film for copper, and a semiconductor device, which enable prevention of copper diffusion even when the thickness of the underlayer film is thinner than that of conventional barrier metals, and which enable superior adhesion to copper wiring film.

[BRIEF DESCRIPTION OF THE FIGURES]

[FIG. 1] Fig. 1 shows a schematic view for illustrating a film-forming apparatus (MOCVD).

[REFERENCE NUMBERS IN THE FIGURES]

la and 1b Source material containers, 3 Heater, 4

Decomposition reactor, 5 Substrate, 7 Gas flow controller, 9 Gas

blowout shower head.

[TITLE OF DOCUMENT] FIGURES [FIG. 1]

[TITLE OF DOCUMENT] ABSTRACT OF THE DISCLOSURE [ABSTRACT OF THE DISCLOSURE]

[PURPOSE] To provide an underlayer film-forming material for copper, a method for forming an underlayer film for copper, an underlayer film for copper, and a semiconductor device, which enable the prevention of copper diffusion even if the thickness of underlayer film is thinner than that of conventional barrier metals, and which enable superior adhesion to copper wiring film.

[MEAN TO SOLVE THE PROBLEMS] an underlayer film-forming material for copper, characterized by comprising a compound represented by the following general formula [I], a method for forming a copper underlayer film using said compound, an underlayer film for copper formed by said method, and a semiconductor device comprising a substrate, said underlayer film and a copper wiring film. General formula [I]: $(R_1R_2)P-(R)_n-Si(X_1X_2X_3)$ [wherein at least one of X_1 , X_2 , and X_3 represents a hydrolysable group; R_1 and R_2 each represent an alkyl group; R represents a divalent linear organic group which is formed of an alkylene group, an aromatic ring, or an alkylene group including an aromatic ring; and n represents an integer of 1 to 6.]

[SELECTED FIGURE] FIG. 1